LOW MOLECULAR WEIGHT PHOSPHORUS-CONTAINING POLYACRYLIC ACIDS AND USE THEREOF AS DISPERSANTS

This invention relates to low molecular weight phosphorus-containing polyacrylic acids, aqueous solutions comprising same, processes for production thereof and also use thereof as dispersants.

Dispersants, especially polyacrylic acids, are widely used in technical operations wherein a solid material is converted into a pumpable dispersion. To ensure wide industrial use, these dispersions, which are also known as slurries, have to have not only good pumpability but also stability in storage (minimal aging) coupled with high solids content. It is desirable for the latter to be raised as high as possible, owing to the high energy and transportation costs. A typical example is the use of aqueous calcium carbonate slurries in the production of graphics papers. While good flow properties on the part of the slurries substantially ensure processability in paper production and/or paper coating, the fineness of the dispersed solids determines the optical properties of the paper produced therefrom, such as the opacity for example. A lower particle size for the same solids content of the slurry results in a higher opacity for the paper produced therefrom. The particle size here is decisively influenced not only by the input of mechanical energy during the wet grinding of the pigment, but also through the choice of dispersant used.

It is known that low molecular weight polyacrylic acids produced by free-radical polymerization have good dispersing properties. The weight average molecular weight (Mw) of these polymers should be <50 000 for good performance. Polyacrylic acids with Mw<10 000 are often particularly effective. To produce low molecular weight polyacrylic acids, chain transfer agents are added as molecular weight regulators during the free-radical polymerization of acrylic acid. These regulators have to be adapted to the polymerization initiator and also to the polymerization process. Examples of known initiators are organic and inorganic percompounds, such as peroxodisulfates, peroxides, hydroperoxides and peresters, azo compounds such as 2,2'-azobisisobutyronitrile and redox systems with organic and inorganic components. The regulators used are frequently inorganic sulfur compounds such as hydrogensulfites, disulfites and dithionites, organic sulfides, sulfoxides, sulfones and mercapto compounds such as mercaptoethanol, mercaptoacetic acid and also inorganic phosphorus compounds such as hypophosphorous acid (phosphinic acid) and its salts (e.g., sodium hypophosphite).

EP-A 405 818 discloses a process for forming polymers from monoethylenically unsaturated monocarboxylic acids and optionally further monomers using sodium persulfate as initiator in the presence of hypophosphite as chain transfer agent, wherein an alkaline neutralizer is present during the polymerization in an amount sufficient to neutralize at least 20% of the acidic groups. The low molecular weight polymers obtained comprise at least 80% of the phosphorus from the hypophosphite. At least 70% of the phosphorus is said to end up within the polymer chain, as dialkyl phosphinate. The polymers thus obtained are used inter alia as laundry detergent additives, dispersants for clay slurries or scale inhibitors for water treatment.

In the exemplary embodiments, acrylic acid is polymerized in water in the presence of hypophosphite as chain transfer agent and sodium persulfate as initiator using the feed method wherein aqueous sodium hydroxide solution is added during the polymerization as a further continuous feed. This gives an aqueous polyacrylic acid having a weight average molecular weight M_w of 2700 g/mol, which comprises 72% of the phosphorus in sodium phosphite as dialkyl phosphinate, 18% as monoalkyl phosphinate and 10% as inorganic salts. A comparative example dispenses with the aqueous sodium hydroxide feed and neutralizes with sodium hydroxide solution only after the polymerization has ended. The product obtained here is an aqueous polyacrylic acid having a weight average molecular weight M_w of 4320 g/mol, which comprises just 45% of the sodium phosphite phosphorus as dialkyl phosphinate, 25% as monoalkyl phosphinate and 30% as inorganic salts.

EP-A 510 831 discloses a process for forming polymers from monoethylenically unsaturated monocarboxylic acids, monoethylenically unsaturated dicarboxylic acids and optionally further monomers, comprising no carboxyl group, in the presence of hypophosphorous acid as chain transfer agent. At least 40% of the phosphorus incorporated in the polymer is present as monoalkyl phosphinate and monoalkyl phosphonate at the end of the polymer chain. The copolymers are used inter alia as dispersants, scale inhibitors and laundry detergent additives.

EP-A 618 240 discloses a process for polymerization of monomers in water in the presence of a water-soluble initiator and hypophosphorous acid or a salt thereof. The process is carried out such that the polymer content at the end of the polymerization is at least 50% by weight. This method provides an increased incorporation of the hypophosphite phosphorus in the polymer. The hypophosphite phosphorus is present in the polymer in the form of dialkyl phosphinate, monoalkyl phosphinate and also monoalkyl phosphonate. No information is provided as to the distribution of the phosphorus. The copolymers are used inter alia as dispersants, scale inhibitors and laundry detergent additives.

EP-A 1 074 293 discloses phosphonate-terminated polyacrylic acid having a molecular weight M_w of 2000 to 5800 g/mol as a dispersant for producing aqueous slurries of calcium carbonate, kaolin, clay, talc and metal oxides having a solids content of at least 60% by weight.

The problem addressed by the invention is that of providing low molecular weight polyacrylic acids having improved dispersing performance.

The problem is solved by a process for preparing aqueous solutions of acrylic acid polymers by polymerization of acrylic acid in feed operation with a free-radical initiator in the presence of hypophosphite in water as solvent, which process comprises

(i) initially charging water and optionally one or more ethylenically unsaturated comonomers,

(ii) continuously adding acrylic acid in acidic, unneutralized form, optionally one or more ethylenically unsaturated comonomers, aqueous free-radical initiator solution and aqueous hypophosphite solution,

(iii) adding a base to the aqueous solution on completion of the acrylic acid feed, wherein the comonomer content does not exceed 30% by weight, based on the total monomer content, wherein

the aqueous hypophosphite solution is added during a total feed time made up of three consecutive feed time spans Δt_I, Δt_{II} and Δt_{III}, wherein the average feed rate in the second feed time span Δt_{II} is greater than the average feed rates in the first and third feed time spans Δt_I and Δt_{III}.

Preferably, the first feed time span Δt_I amounts to 30 to 70% of the total feed time.

Preferably, the second feed time span Δt_{II} amounts to 5 to 25% and more particularly 5 to 15% of the total feed time.

Preferably, the third feed time span comprises two subsidiary feed time spans Δt_{IIIa} and Δt_{IIIb}, wherein the average feed rate during the first subsidiary feed time span Δt_{IIIa} is not less